ARL Mediation of Gun Tube Erosion

Weapons and Materials Research

Trial, Error, and Hydrogen Diffusion

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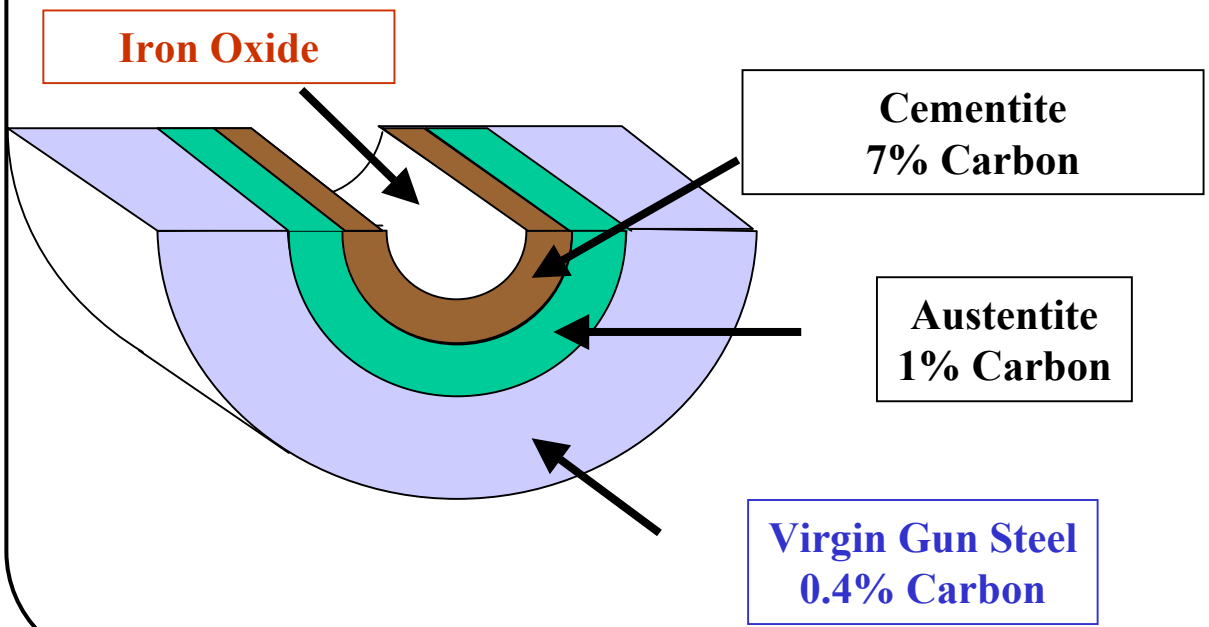
Gun Tube Wear and Erosion

BARREL SEGMENT

PROBLEM

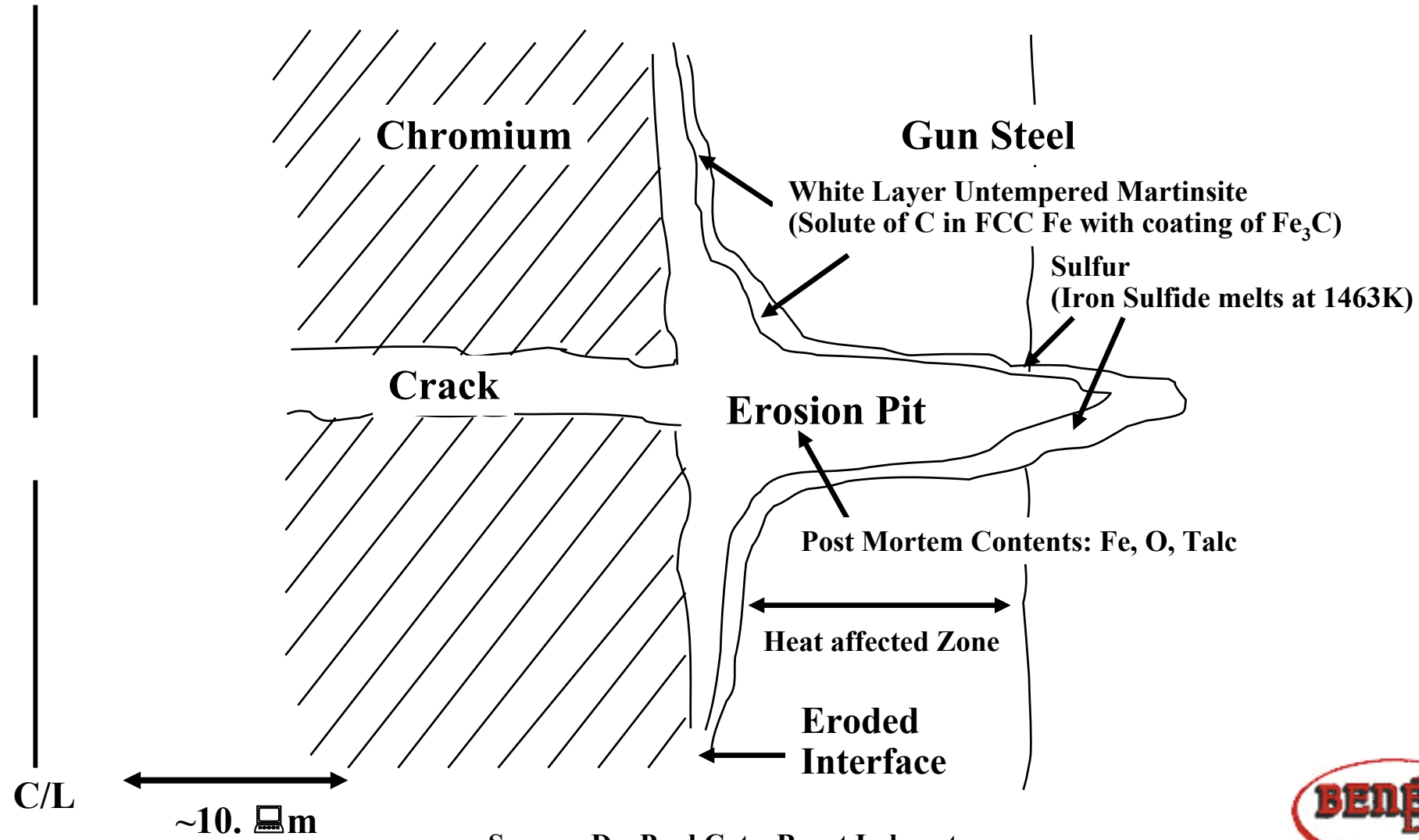
Gun Firing → Carburization, Oxidation, Sulfurization, …

Carburization, Oxidation, … → Erosion



Erosion Pockets Beneath Chrome
120 mm M256 Cannon

Weapons and Materials Research



Source: Dr. Paul Cote, Benet Laboratory

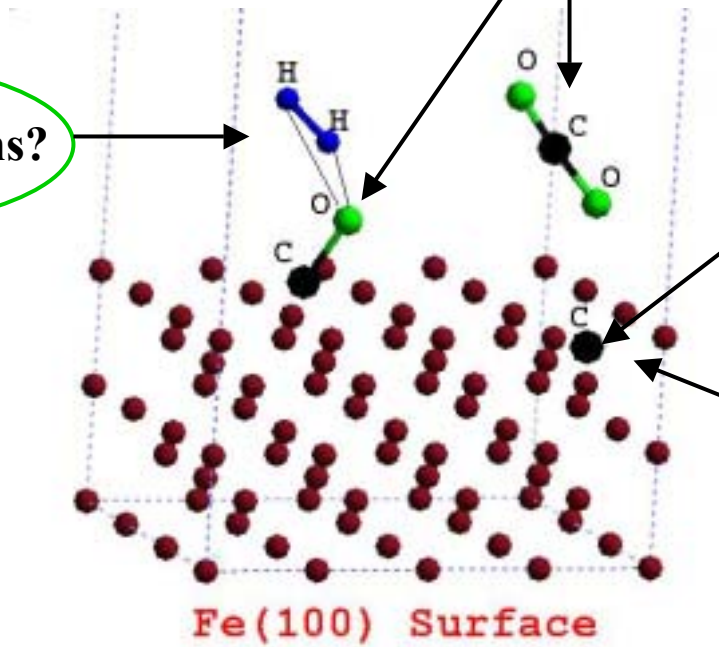
Model Chemical Reactions and Conditions Responsible For Gun Steel Degradation

Sources of Carbon, Oxygen, etc?

Mitigating Reactions?

Diffusion Rates?

Lattice Re-arrangement?



TEMPERATURE?

CONCENTRATION?

PRESSURE?

GENERAL RESEARCH PLAN

QUANTUM MECHANICS

- Correlate - Energy *vs* Atomic/Molecular Structure

CLASSICAL MECHANICS/DYNAMICS

- Predict Rate Constants for Surface Rxn's
- Predict Diffusion Rates of Atoms into Steel

KINETIC MODELS

- Predict Rates for Iron Oxide/Carbide/Nitride/… Formation *vs* Propellant Combustion Product Composition
- Predict Rates FOR CHEMICAL EROSION of GUN TUBES !!!

Theoretical Chemistry/Physics Approaches

I. "First Principles" Quantum Mechanical Approach

A. All approaches are based on Density Functional Theory (DFT)

B. All calculations use Pseudo-Potentials to replace core electrons

C. Slab Models: 3-D Periodic Boundary Conditions to Reproduce Bulk Effects

- Pseudo-Potential Planewave Method (CASTEP and VASP)

(Byrd/Sorescu/CFC)

D. Cluster Models (AOs) QC: Direct MD with Gaussian98 (Ishikawa)

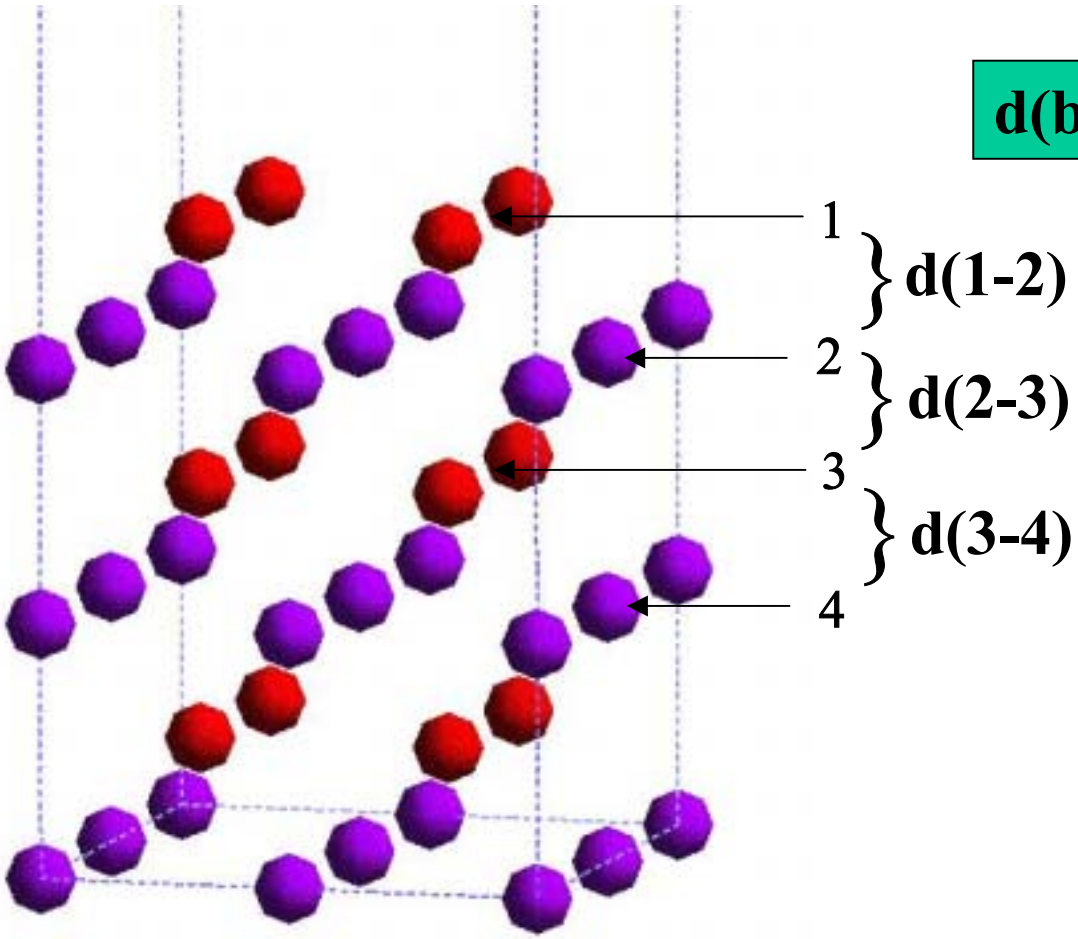
II. Classical Molecular Dynamics Simulations Approach

- Embedded Atom Model (EAM): Farkas-Simonelli (Hurley)

Fe BCC Optimized Bulk Properties and Properties of CO

Property	Experiment	Theory	
		PP-PW (CASTEP)	PP-PW (VASP)
Lattice Constant (Å)	2.8664	2.8151(1.8%)	2.8653(0.0%)
Bulk Modulus (GPa)	170	178(4.7%)	161(5.2%)
Effective Magneton Number (n_b)	2.22	2.20(1.0%)	2.86(5.4%)
Saturation Magnetization (M_0)	1750	1809(3.3%)	1876(7.2%)
CO			
R_e(C-O) Å	1.128	1.144 (1.4%)	1.145 (1.5%)
Vibr. Freq. cm^{-1}	2143 cm^{-1}	2228 (3.5%)	2174 (1.5%)
Bond Energy	259.3 kcal/mol	252.9 (2.5%)	253.6 (2.2%)

THEORETICAL PREDICTIONS for RELAXATION of SURFACE LAYERS



Fe(100) Surface 1x1 Unit Cells

$d(bulk)^{Theory} = 1.413$ Å

EXPERIMENT

$\Delta d(1\text{-}2) = -5 \pm 2\%$

$\Delta d(2\text{-}3) = +5 \pm 2\%$

NOTE

5% ≈ .070 Å

1% ≈ .014 Å

Fe (100) RELAX TOP TWO LAYERS

Experimental Error ±2%

Layer Separation	NUMBER OF LAYERS IN SLAB							
% Change	4L	5L	6L	7L	8L	10L	12L	Exp.
d(1-2)	-2.7	-4.3	-2.6	-3.8	-4.2	-4.0	-3.9	-5.0%
d(2-3)	4.0	3.1	3.1	2.7	2.7	3.0	2.7	5.0%
ΔE (eV)	0.011	0.013	0.008	0.010	0.011	0.011	0.010	

1% ≈ .014 Å

Table 4. Relaxed Fe (111) surface structure for a (1x1) super-cell *versus* slab Thickness and number of layers being relaxed.

SLAB THICKNESS VERSUS Δd (Relax Top 4 Layers)

Layer Separation		NUMBER OF LAYERS IN SLAB 7L	8L	9L	10L	11L	12L	13L	Exp.*
% Change	d(1-2)	-2.0	-1.4	-4.8	-5.1	-3.4	-1.9	-3.9	-16.9
	d(2-3)	-18.0	-22.9	-17.9	-17.9	-17.6	-19.1	-19.6	-9.8
	d(3-4)	14.1	16.8	12.0	12.7	11.1	11.2	13.8	4.2
	d(4-5)	0.8	0.4	2.6	2.0	1.4	1.6	0.2	-2.2

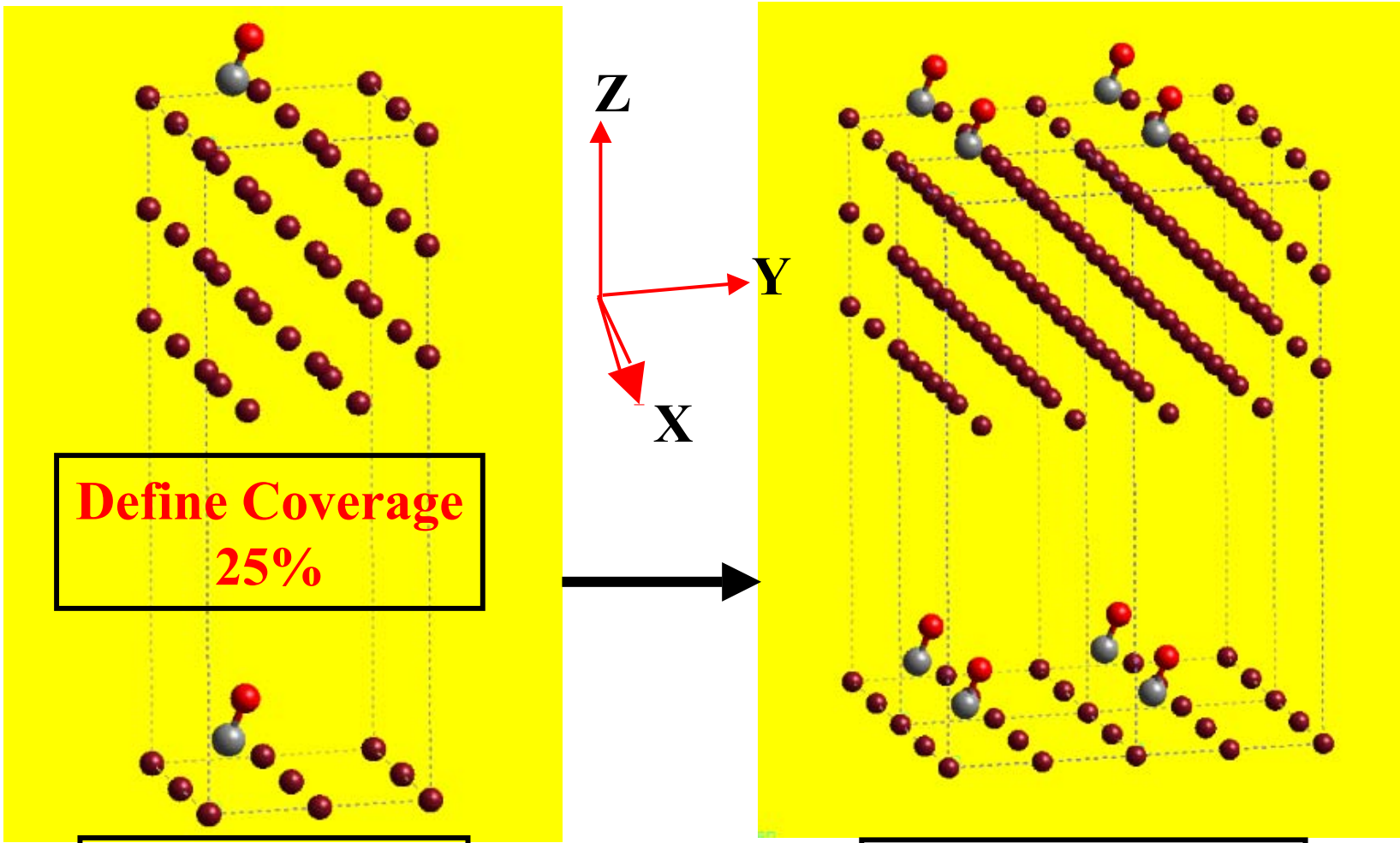
Experimental Error: ±3-4%

TEST - RELAX TOP 5 LAYERS

MODEL	d(1-2)	d(2-3)	d(3-4)	d(4-5)	d(5-6)
10 Layers, Relax 5	-5.9%	-17.1%	12.0%	-1.0%	2.8%
Experiment	-16.9%	-9.8%	4.2%	-2.2%	

* Ref. 44

Model of SLAB in BCC Crystal Structure



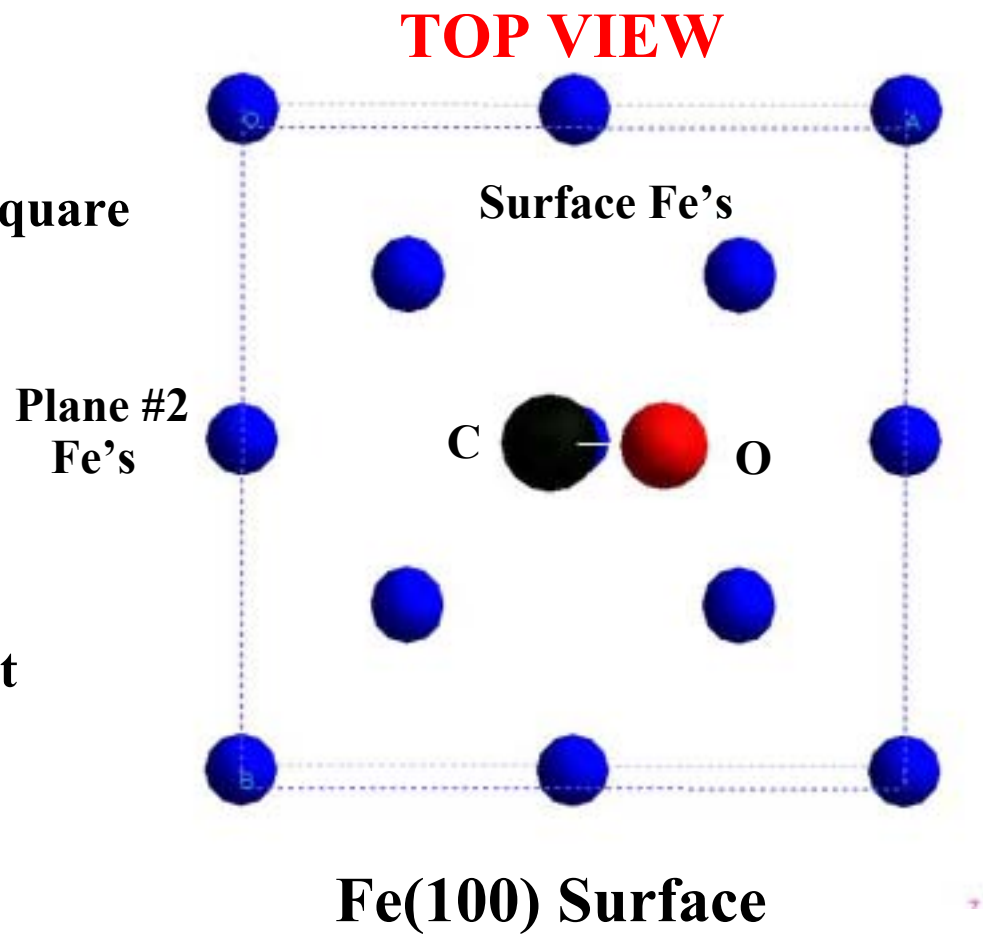
CO on Fe(100) SURFACE

EXPERIMENT

- Predicts CO bisects surface square with C above Fe in Plane #2.

THEORY(PP-PW)

- Agrees well with Experiment



Fe (111) Surface

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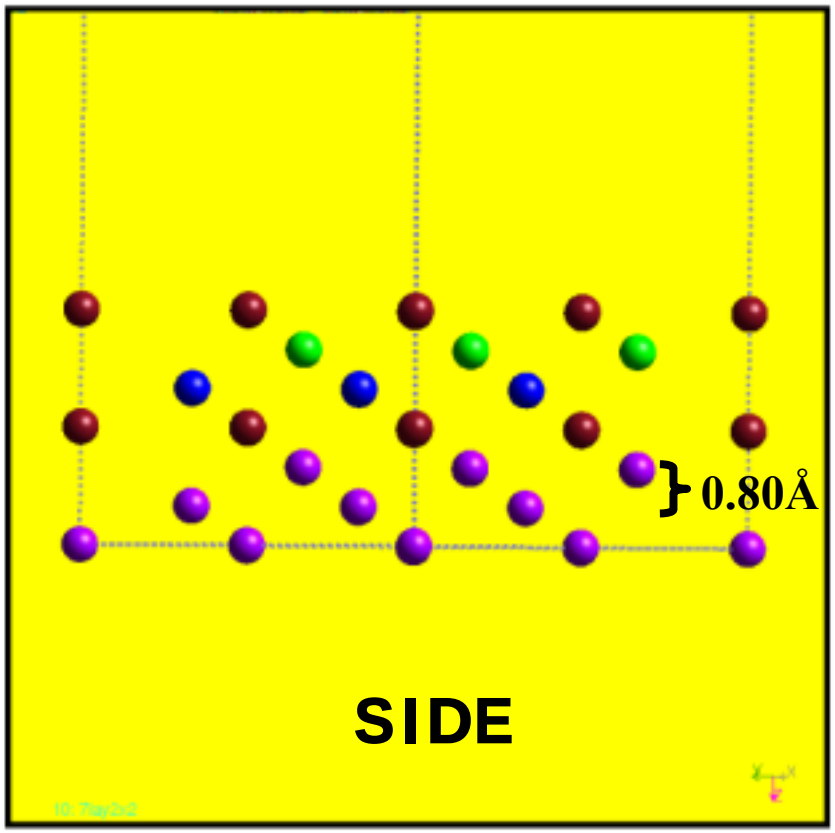
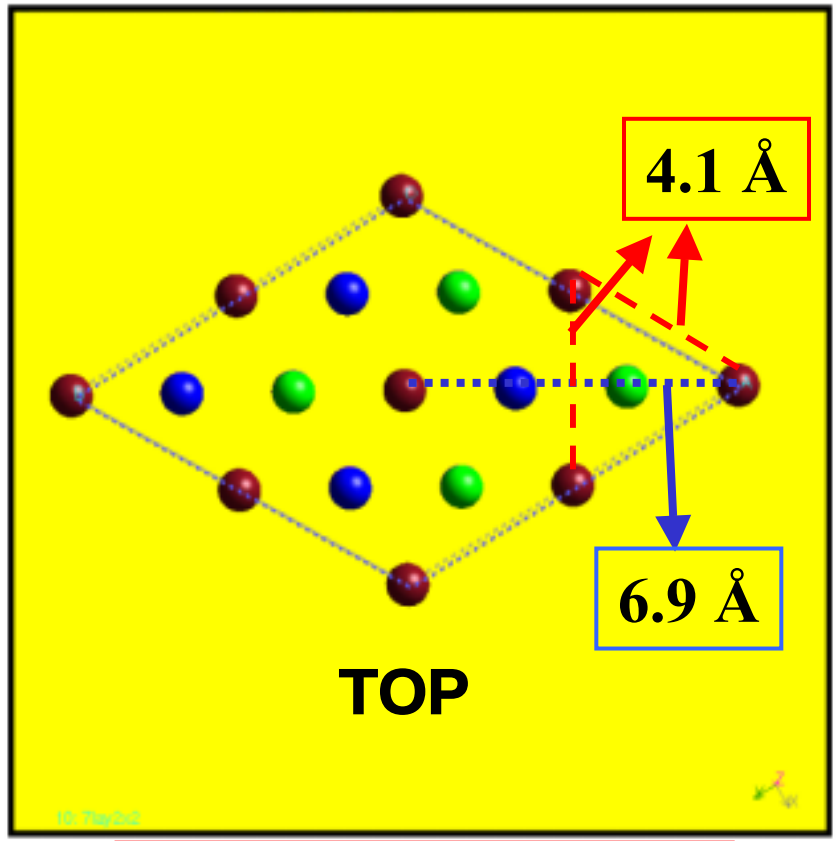
Fe (111) Surface for 2x2 Unit Cells/Supercell





(111) Layers Spacing in Bulk = 0.80 Å

In (100): 2.9Å x 4.1Å

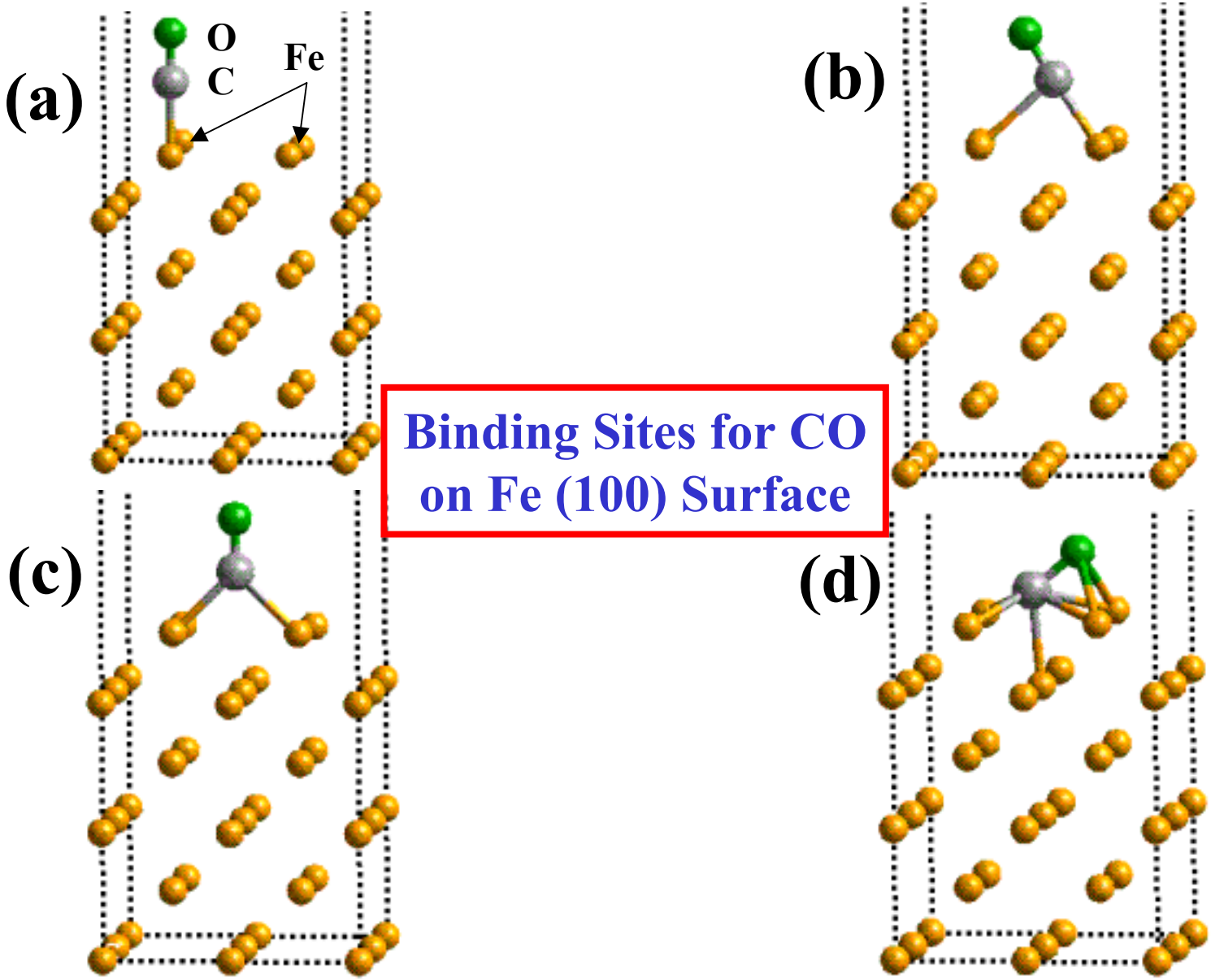
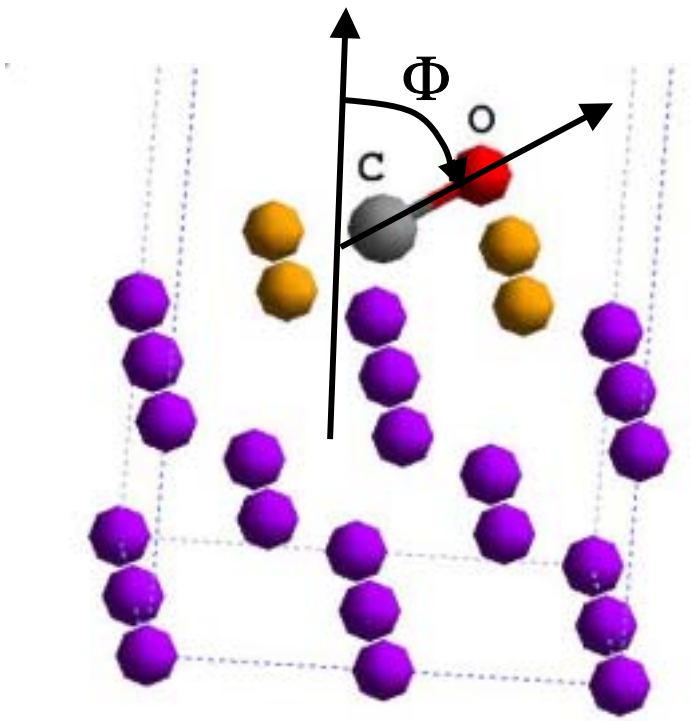


Figure 1. Adsorption config.s of CO on Fe(100) surface: (a) on-top configuration; (b) 2-fold bridge tilt configuration; (c) 2-fold vertical configuration; (d) 4-fold hollow sites configuration.

Optimize Structure for Carbon Monoxide on Relaxed Fe(100) Su

(Yellow atoms = Iron Surface Atoms)
(Purple Atoms = Iron Subsurf. Atoms)
6 Layer Slab/K-pts = 4x4x2



CO on Fe(100) Surface

Property	Experiment	Theory
R(C-surface)	0.60 ± 0.1 Å or ? 0.20 ± 0.1 Å	0.58 Å
Φ	(45°±10, 55°±2)	50°
R(C-O)	R > 1.20 Å (?) gas phase = 1.13	1.32 Å
R(C-Fe) Nearest Fe	2.04 Å or ? 1.64 Å	1.97 Å
ΔH Adsorp. Kcal/mol	-26.2 (-30 → -36)	– 43.8

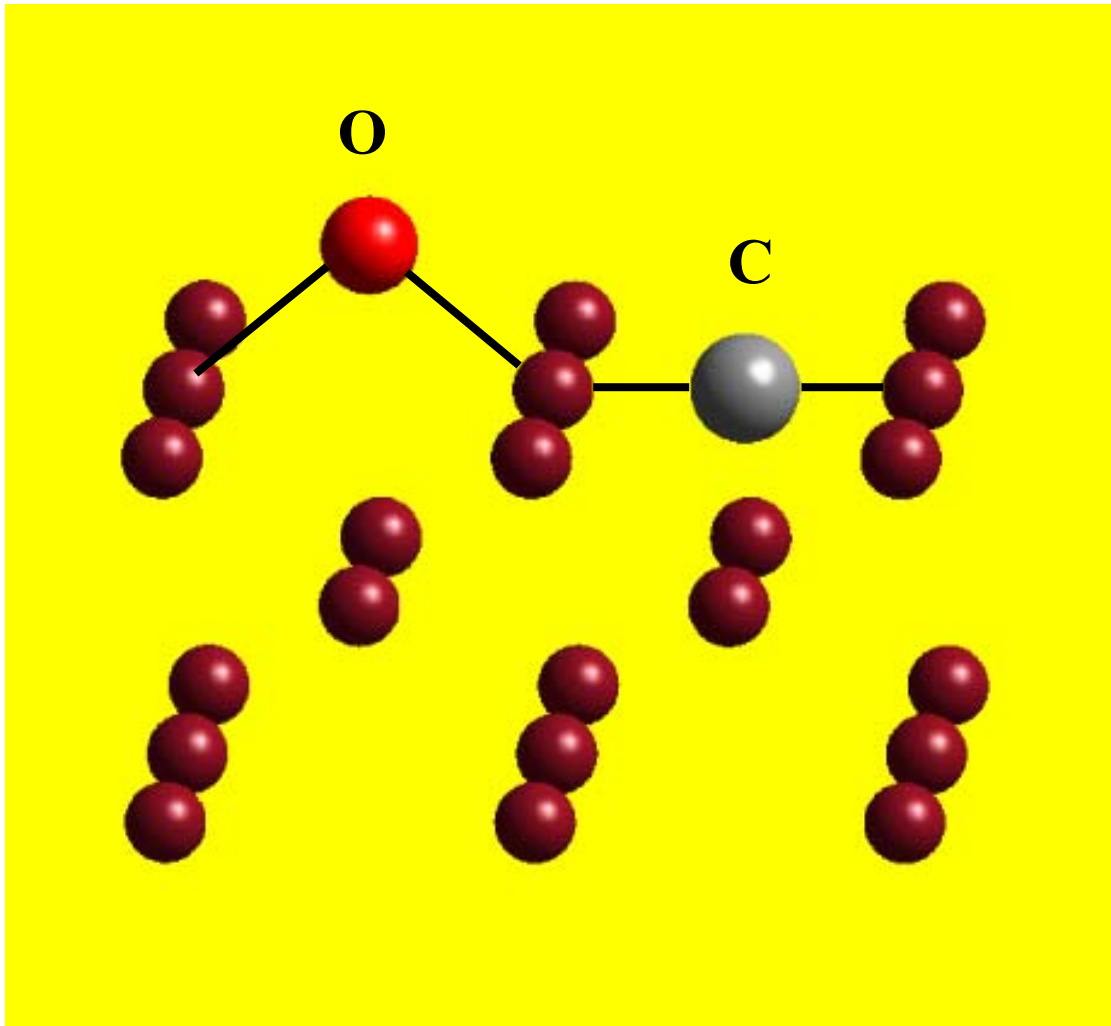
Assumed Pre-exponential of 10^{13} s^{-1}, later experiments recommend $10^{15\text{-}18}$ s^{-1}

BINDING ENERGIES - CO, C and O atoms on Fe 2x2 (100) SURFACE

Location	% Coverage	R(Fe-X)	R(X-Surf)	E_{ads} (kcal/mol) Theory	Exp.
		CO			
1-Fold	25			-32.1	-17-23
2-Fold	25			-32.3	-22-28
4-Fold	25			-43.8	-30-36
		C atom			
1-Fold	25	1.605		-118	
2-Fold	25	1.73/1.74		-154	
4-Fold	25		0.396	-186	
		O atom			
1-Fold	25	1.64		-111	
2-Fold	25	1.83/1.83		-132	
4-Fold	25		0.613	-145	

1. C bonds more strongly than O
2. For Both C and O: Bonding Strength: E(4F) > E(2F) > E(1F)
3. 2-Fold: C Embeds Into Lattice: ∠ Fe-C-Fe = 172°

Structure of Carbon and Oxygen on (100)



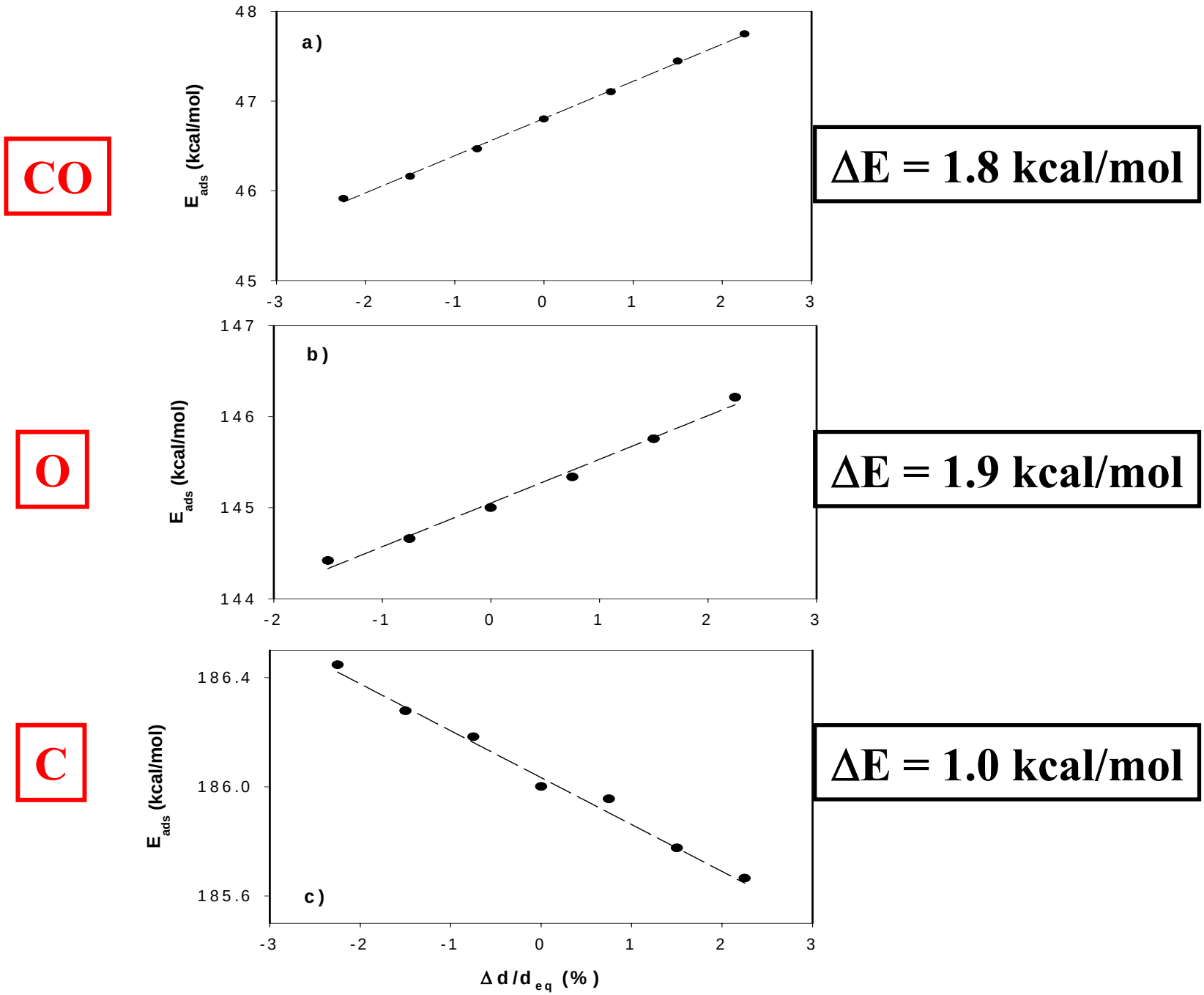

CO
O
C
a)
b)
c)
E_{ads} (kcal/mol)
$\Delta d/d_{eq}$ (%)
48
47
46
45
147
146
145
144
186.4
186.0
185.6
-3
-2
-1
0
1
2
3
ΔE = 1.8 kcal/mol
ΔE = 1.9 kcal/mol
ΔE = 1.0 kcal/mol

Figure 3

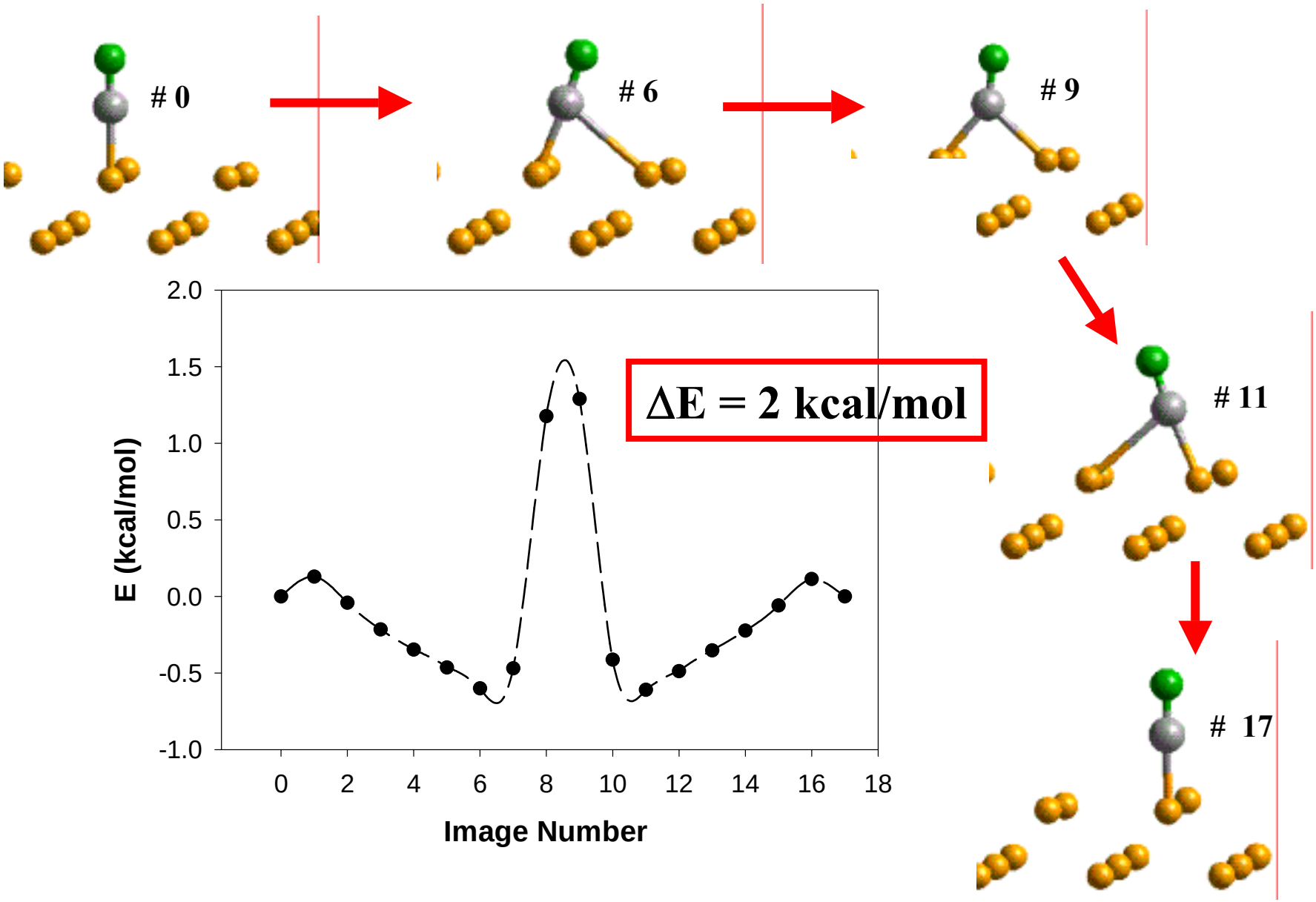


Figure 4. Potential energy surface for diffusion of CO from an on-top site to a neighbor on-top site. Path is through the bridge-tilted configurations.

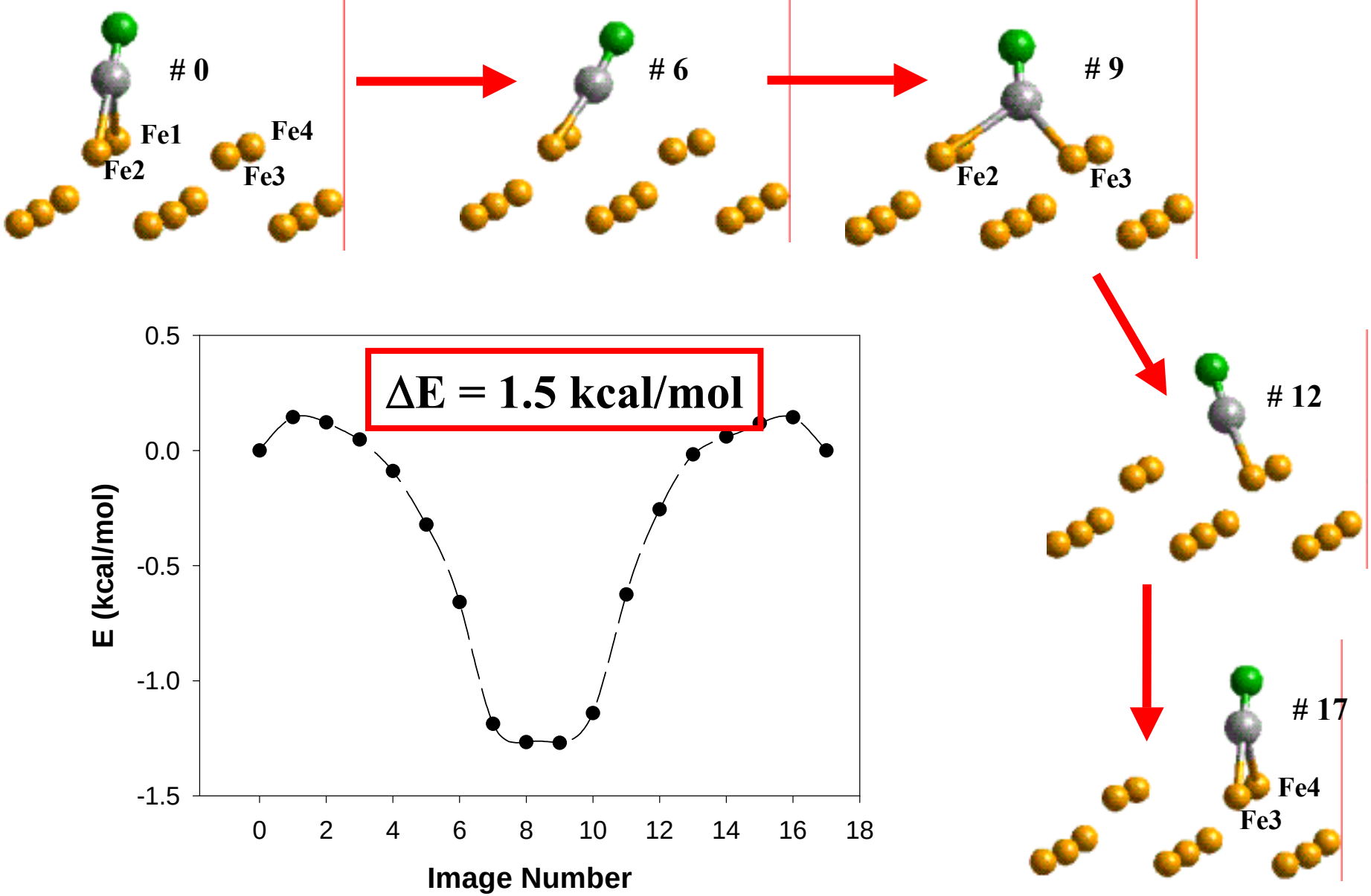


Figure 6. Potential energy surface for motion of CO from a bridge-tilt configuration between Fe1-Fe2 to bridge-tilt between Fe3-Fe4 along a path involving bonding to Fe2-Fe3 atoms.

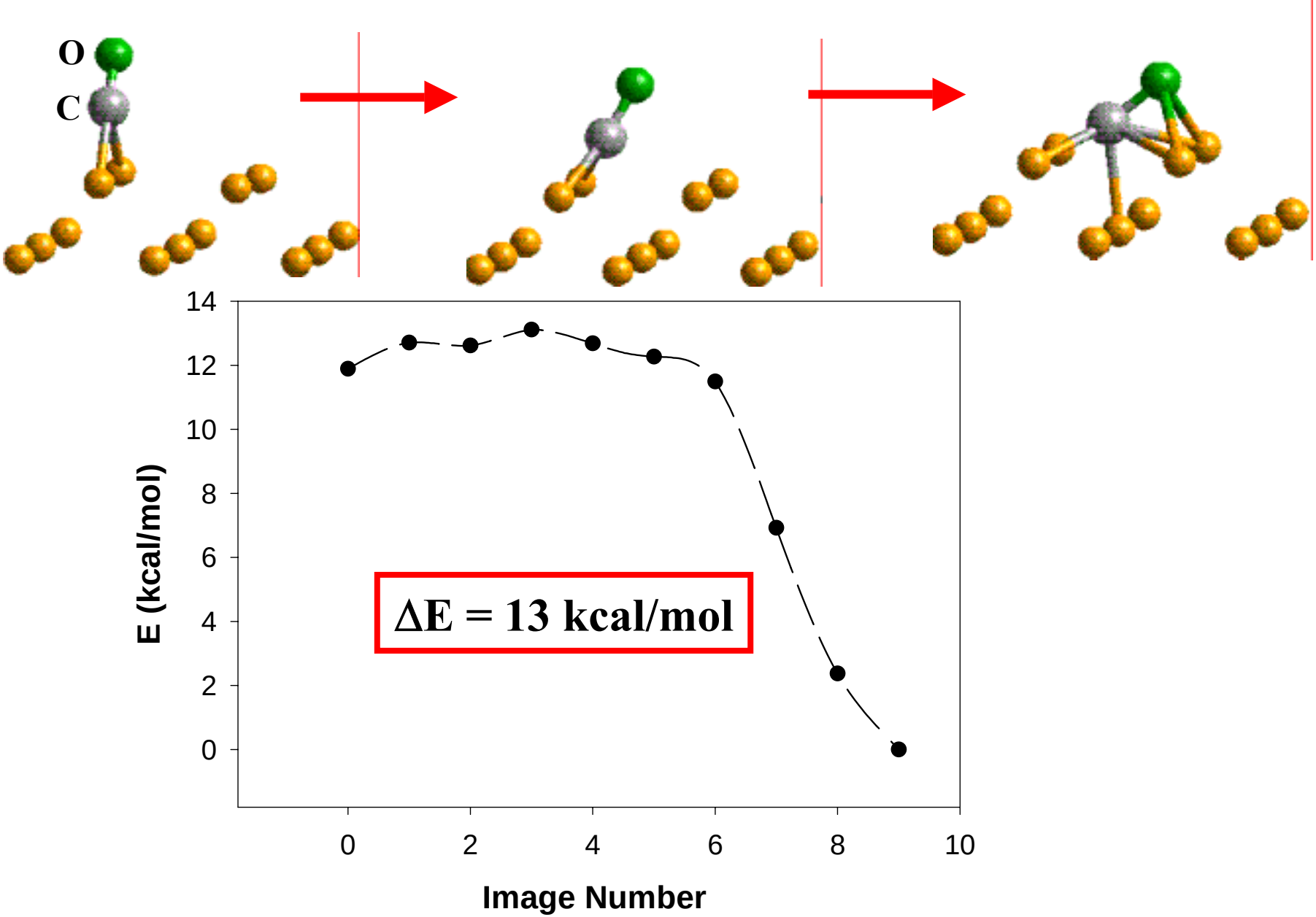


Figure 5. Potential energy surface for diffusion of CO molecule from a bridge-tilt configuration to a 4-fold hollow site.

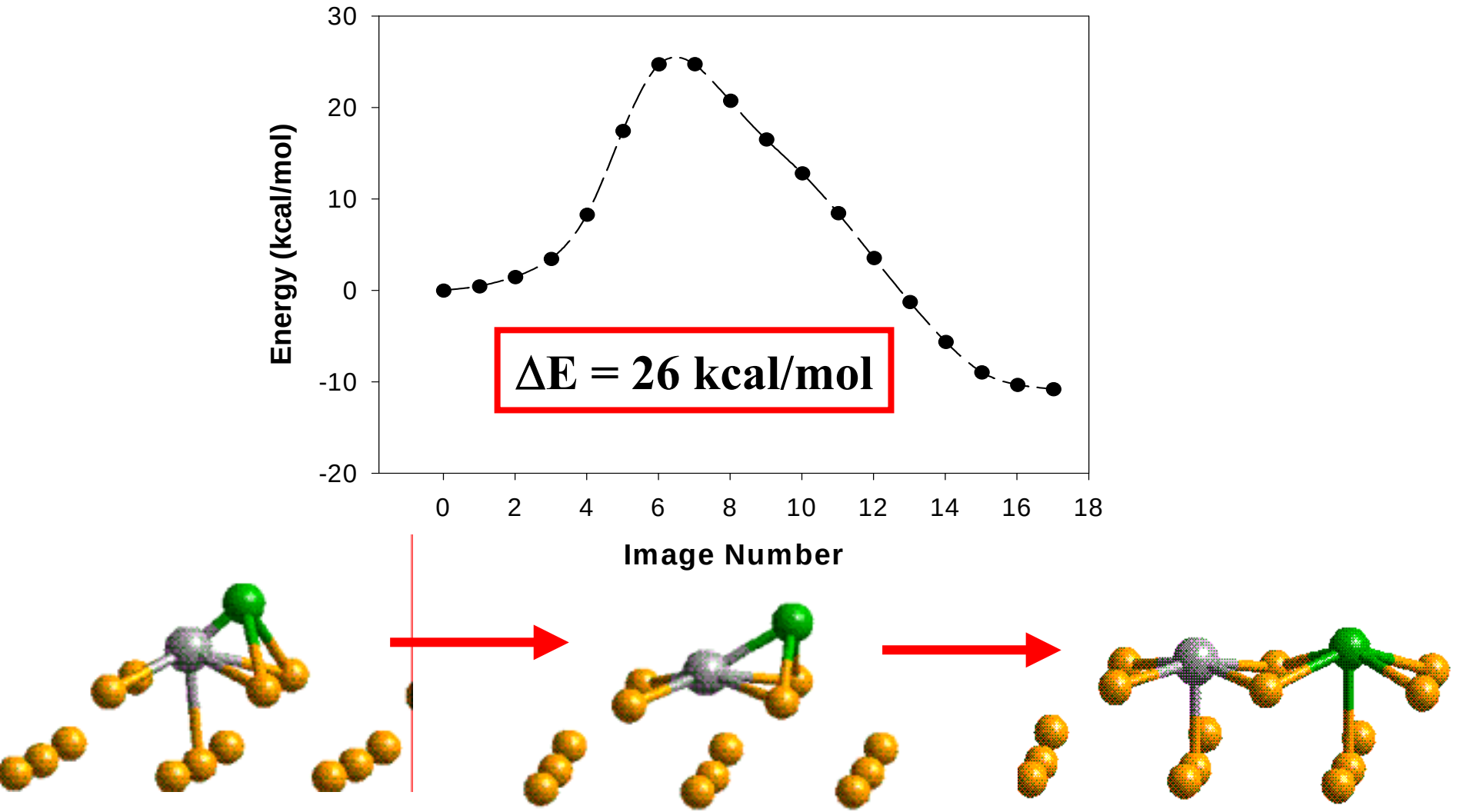


Figure 7. Potential energy surface for dissociation of CO at 4-fold hollow site. Final configuration corresponds to C and O atoms adsorbed at two different 4-fold hollow sites.

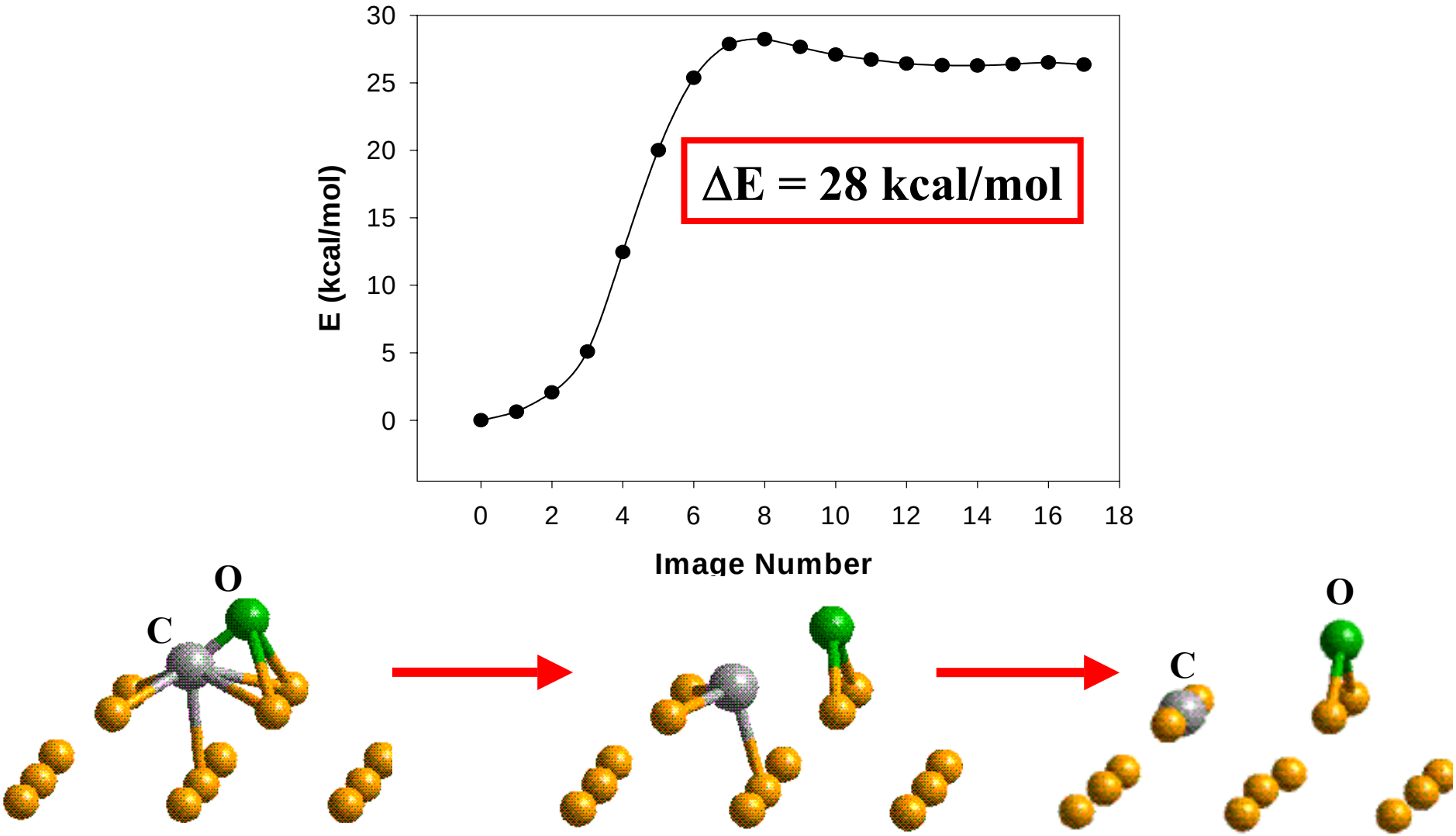
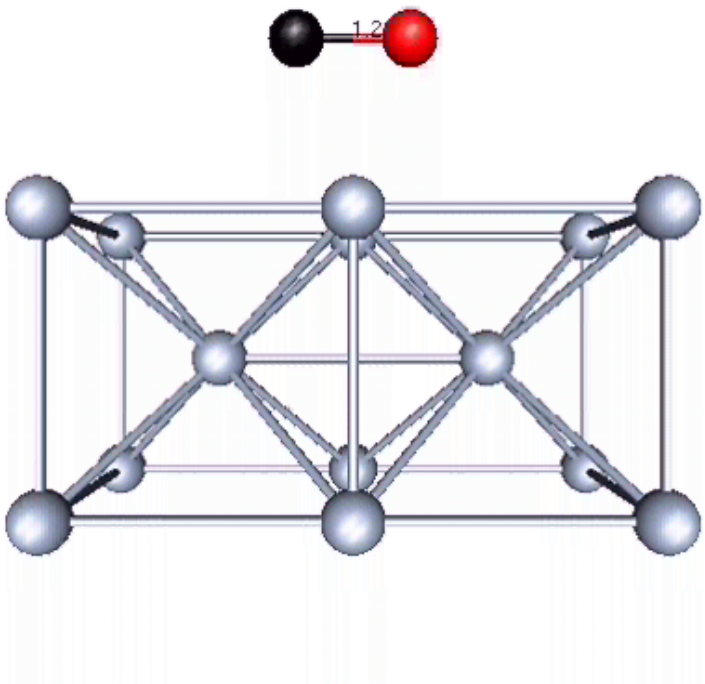
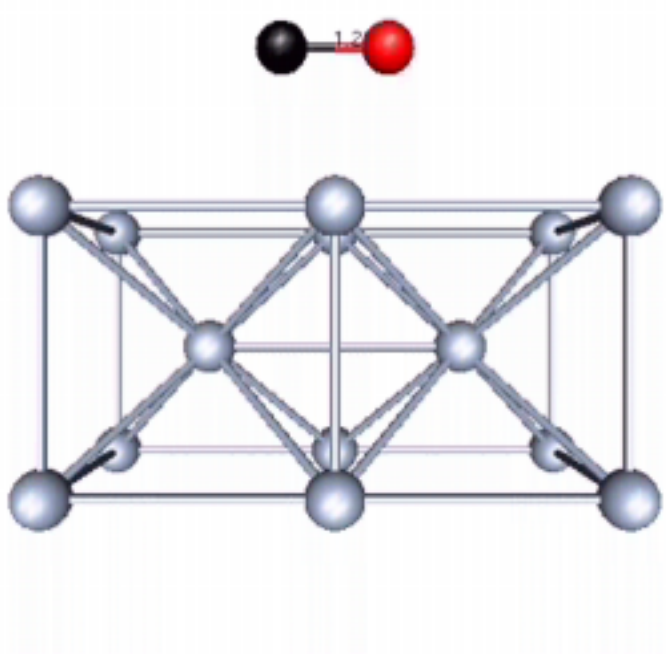


Figure 8. Potential energy surface for dissociation of CO at the 4-fold hollow site. Final configuration is C and O atoms bound at two opposite 2-fold sites.

Quantum Mechanical Direct MD Simulations CO Reacting on Fe Cluster



Non-Reactive Collision
E_{kin} = 8 kcal/mol



Reactive Collision
E_{kin} = 16 kcal/mol

Molecular Dynamics – Prior Fit for Iron

Tersoff

Note the bond order (BO) term takes bond directionality into account.

Tersoff-type potentials are frequently used for lattice systems involving covalent networks like silicon crystals. So…. Iron?

Highly parameterized (~16 terms?)

fitted to reproduce many experimental properties, including BCC elastic moduli, relative energies of FCC and HCP, and (111) free surface energy

Resulted in correct energetics, poor iron free surface spacings

Attempted to reparameterize to give correct Fe(111) free surface spacing

Gave up

EAM

Embedded Atom Potentials are frequently used for metals (including iron)

They take the form:

$$E = \tfrac{1}{2} \Sigma V(r_{ij}) + \Sigma F(\rho_i)$$

$$\rho_i = \Sigma \varphi(r_{ij})$$

Where V is a pair potential
F is the embedding function
ρ is the total electronic density of atom i due to surrounding atoms
Φ is the electron density on atom i due to atom j

EAM

Used EAM formulation of Farkas et al. adapted from Simonelli, Pasianot, and Savino, *Materials Res. Soc. Symp. Proc.*, 291, 567 (1993)

Used by engineers for molecular statics simulations of fracture

Results on Bulk Fe:

- **BCC lower in energy than FCC (good)**
- **BCC lattice constant of 2.8664 Angstroms (expt 2.8665 Ang good)**
- **FCC lattice constant of 3.6408 Angstroms**
- **BCC lattice thermal expansion (calculate expansion of cell w/increasing temp) gets lattice constants at higher temps w/in 1%**

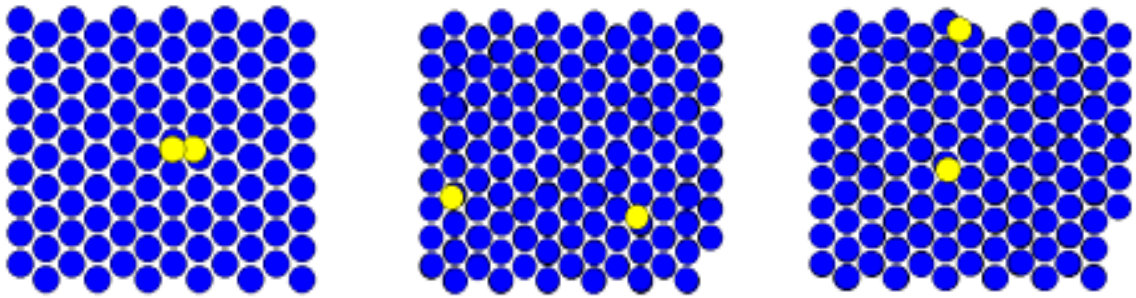
{100} Surface Relaxations

Bulk spacing 1.433 Ang	Expt	Present Theory
d12	~1.36 (-5%) (1.41??)	~ 1.44 (+1%)
d23	~1.50 (+5%)	~ 1.42 (-1%)
d34	1.433	~ 1.435
d45	1.433	~ 1.433
d56	1.433	~ 1.433
d67	1.433	~ 1.433
d78	1.433	~ 1.433

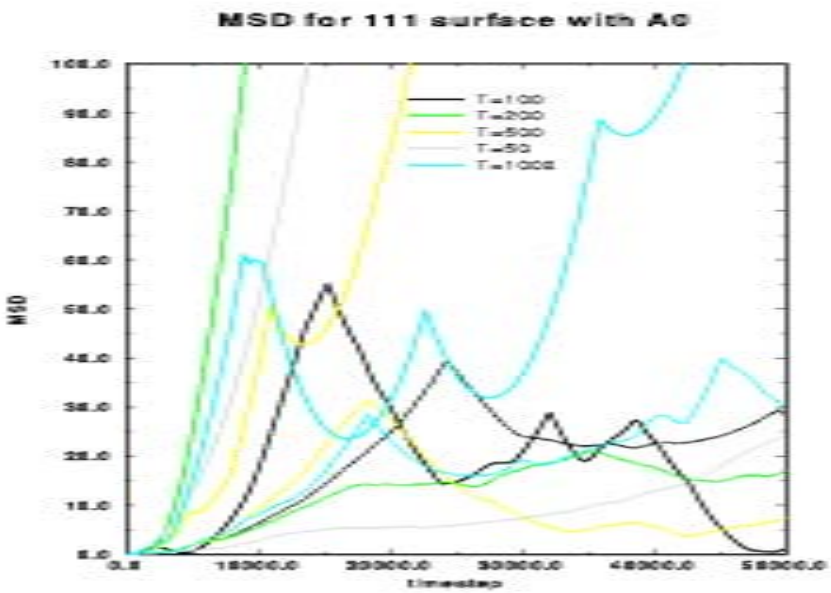
{111} Surface Relaxations

Bulk spacing 0.827 Ang	Expt	Present Theory
d12	~ 0.687 (-16.9%)	~ 0.800 (-3.3%)
d23	~ 0.746 (-9.8%)	~ 0.726 (-12.2%)
d34	~ 0.862 (+4.2%)	~ 0.886 (+7.1%)
d45	~ 0.809 (-2.2%)	~ 0.823 (-0.5%)
d56	0.827	~ 0.804 (-2.7%)
d67	0.827	~ 0.845 (+2.1%)
d78	0.827	~ 0.823
d89	0.827	~ 0.822

Molecular Dynamics – Farkas EAM

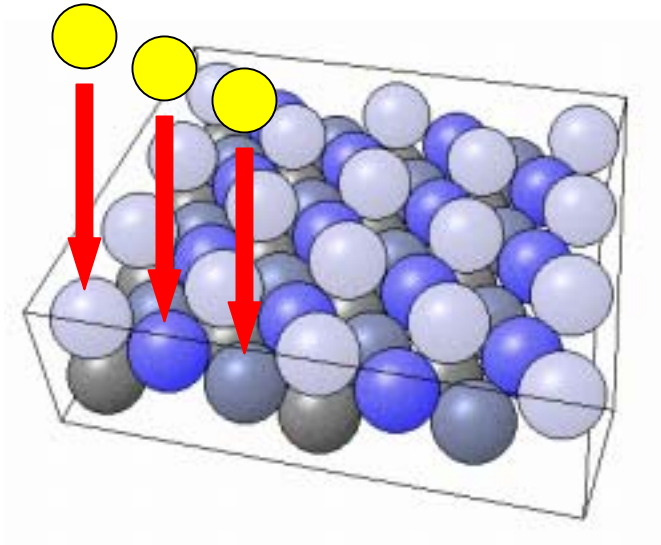


0 timestep ⟶ 24700 timestep ⟶ 50000 timestep



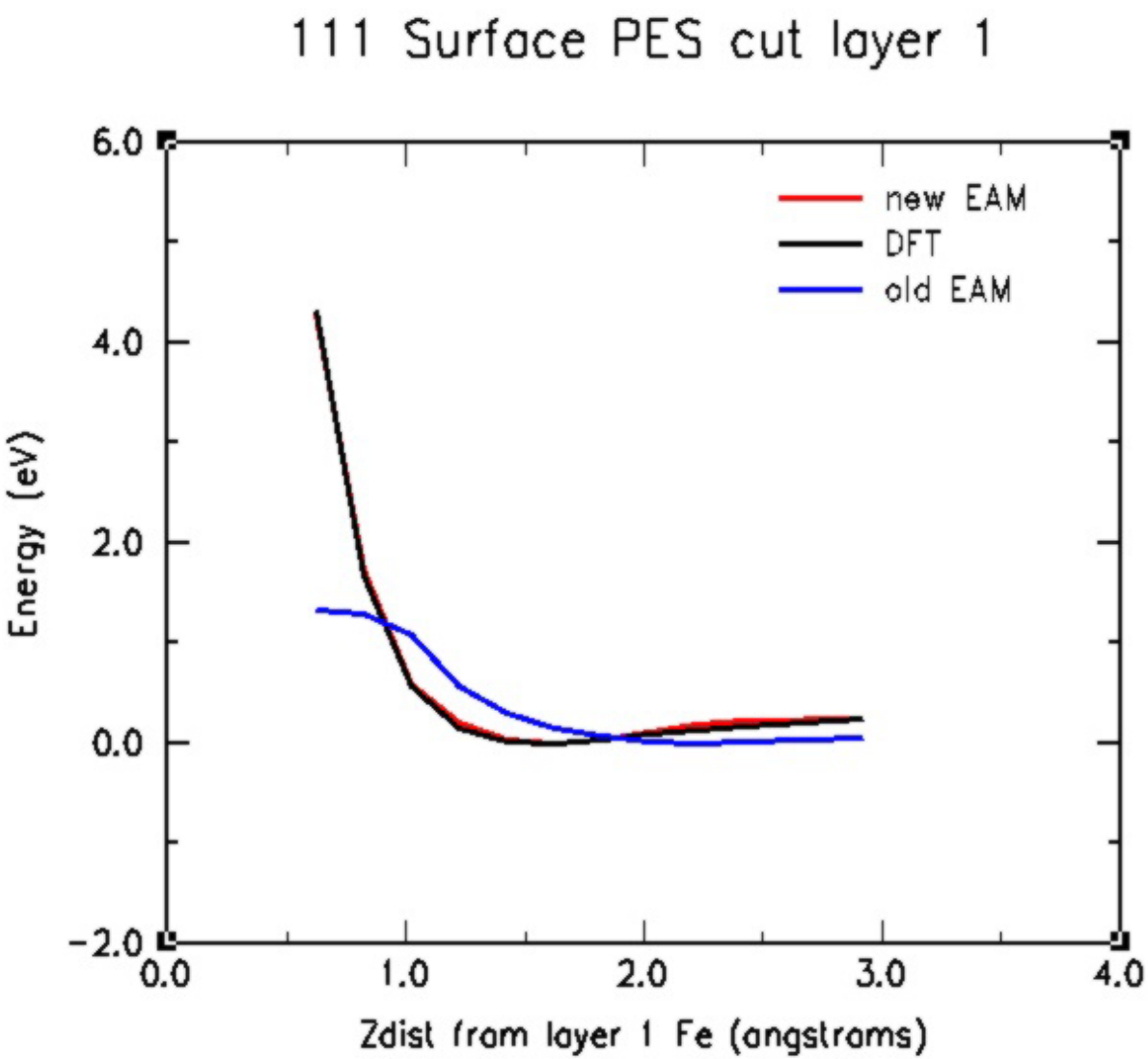
111 Surface with 1 H2

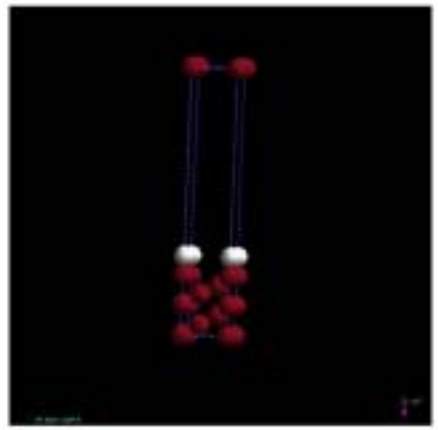
Molecular Dynamics DFT fit

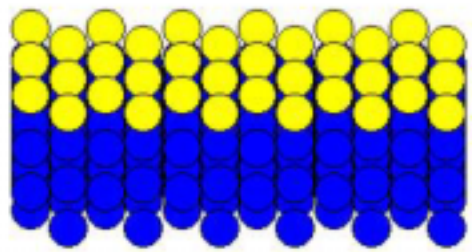


Fe seems usable, Fe-H and H-H are broken
Get series of cuts to PES (potential energy surface) by DFT and refit Fe-H. Start with 111 surface

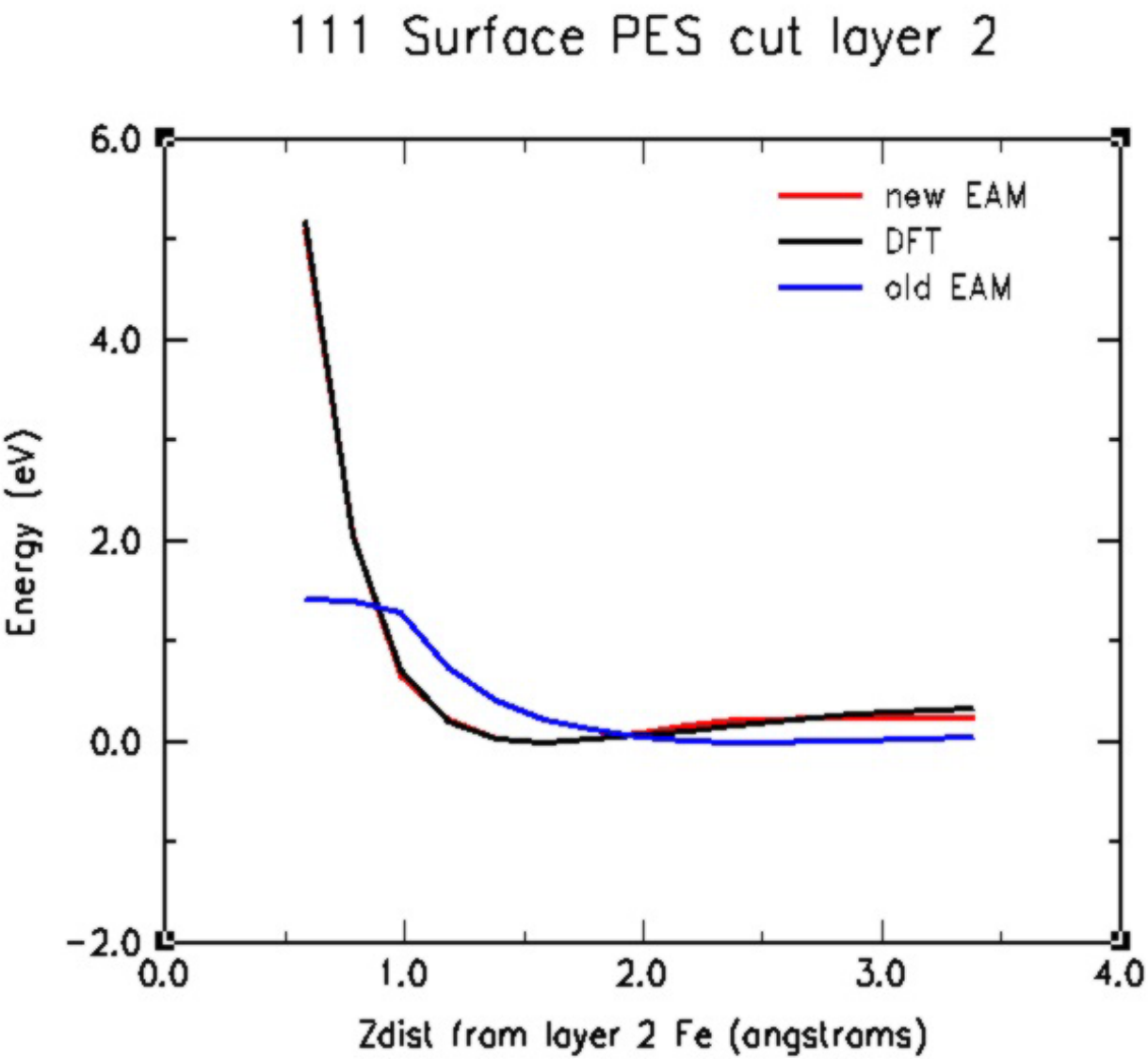
Potential Energy Surface Cut- 111 Surface Layer 1

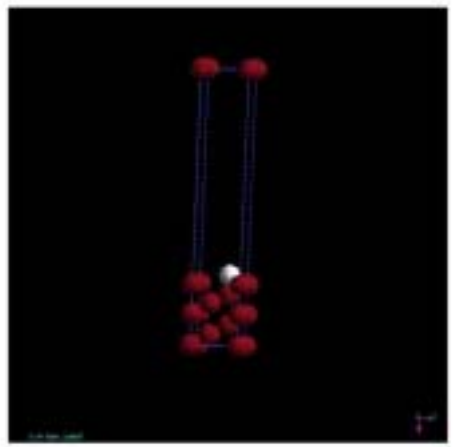


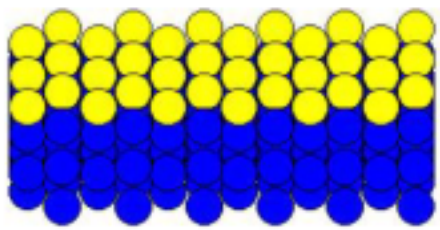




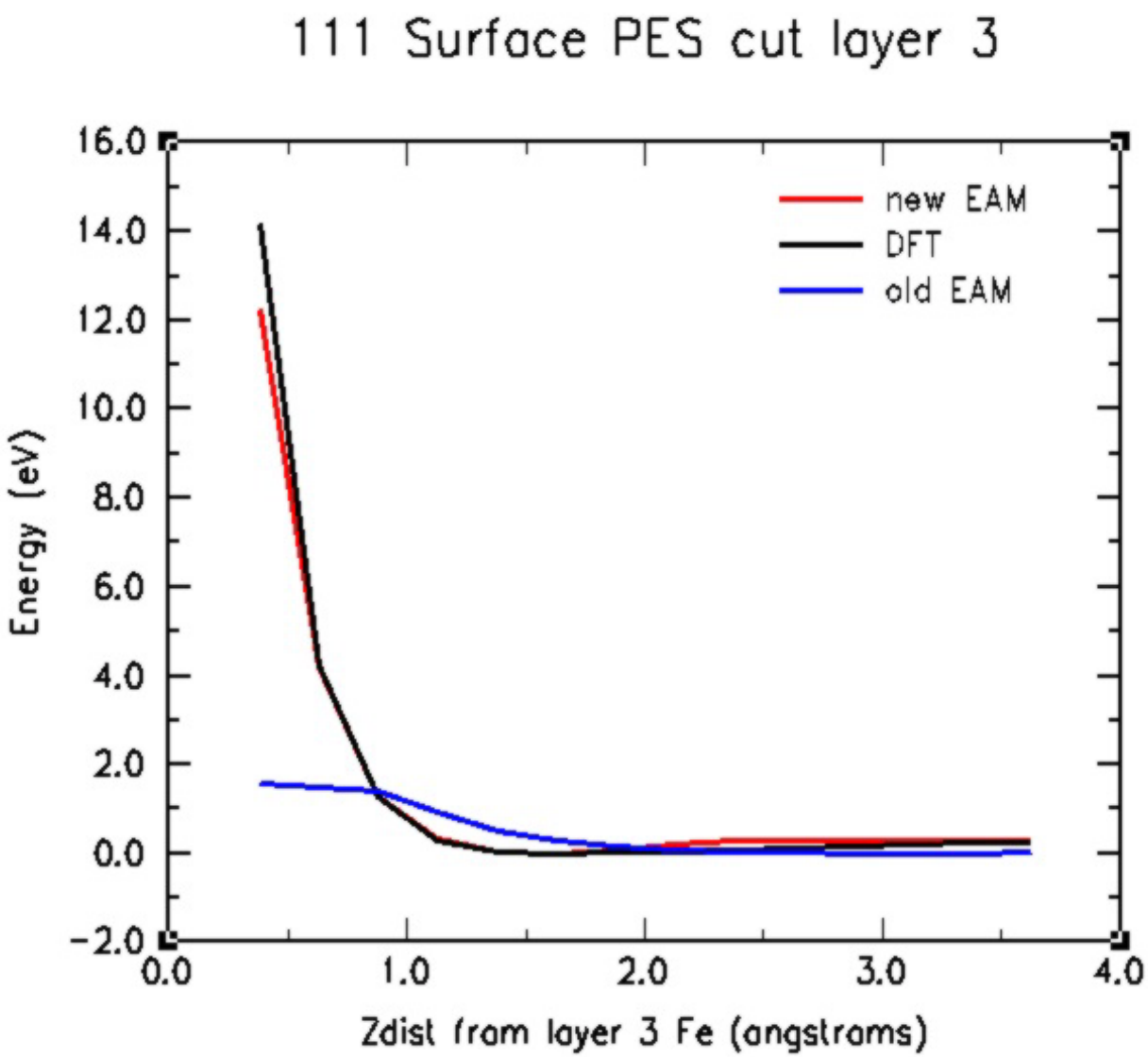
Potential Energy Surface Cut- Farkas Layer 2

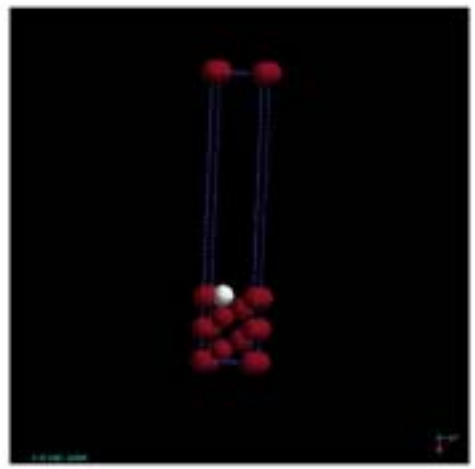


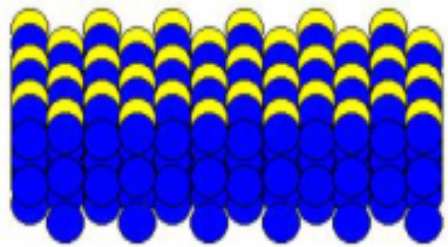




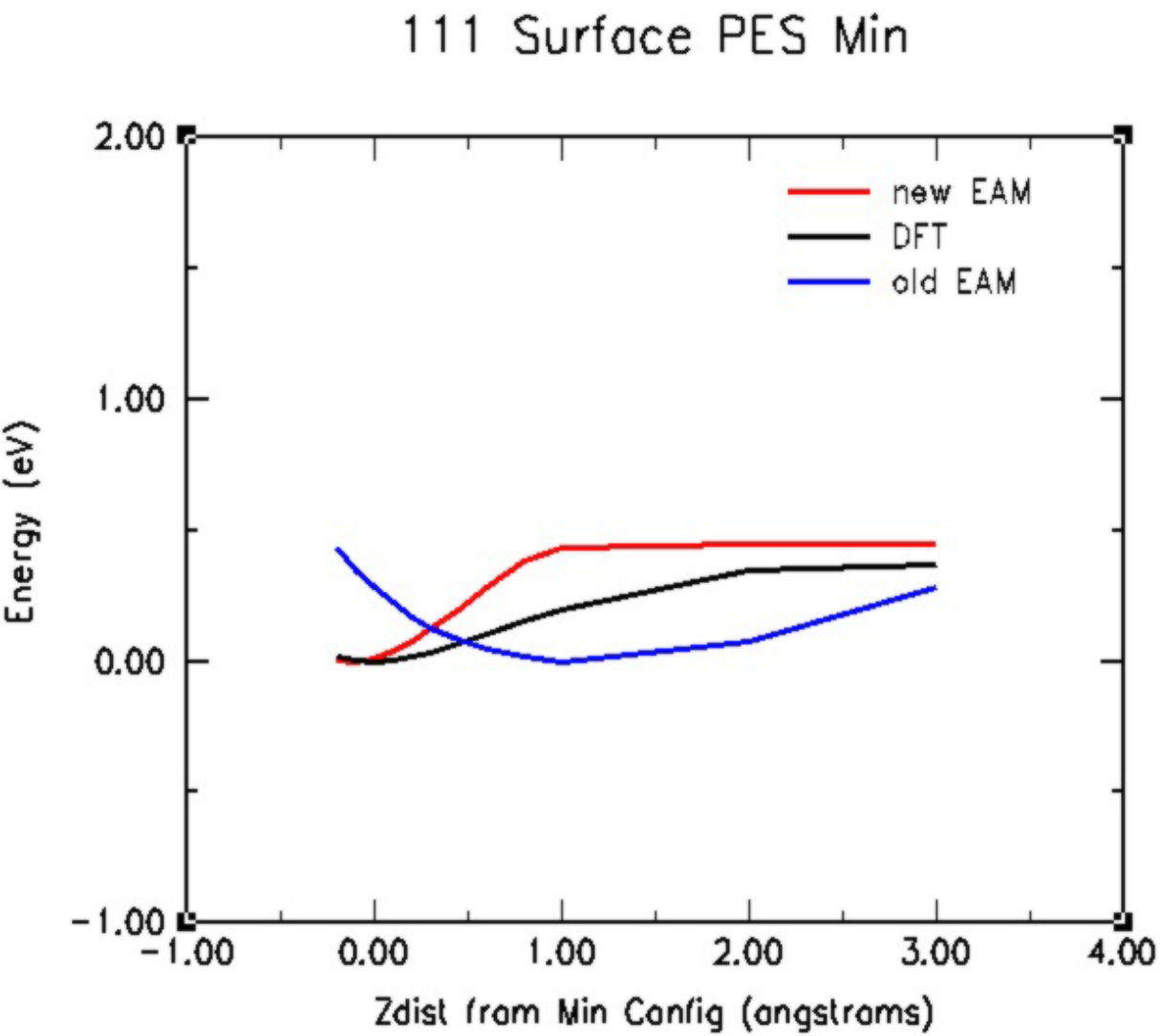
Potential Energy Surface Cut- Farkas Layer 3

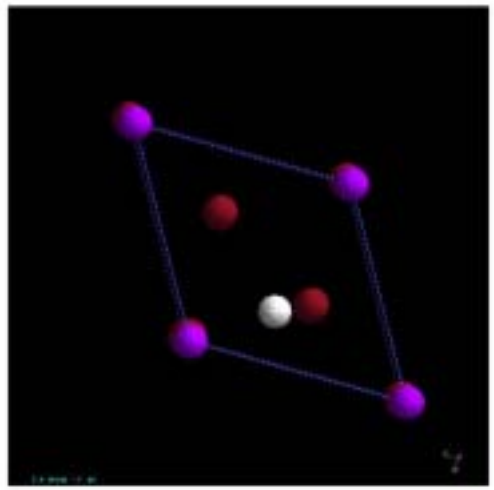


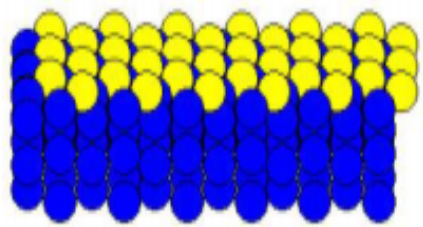




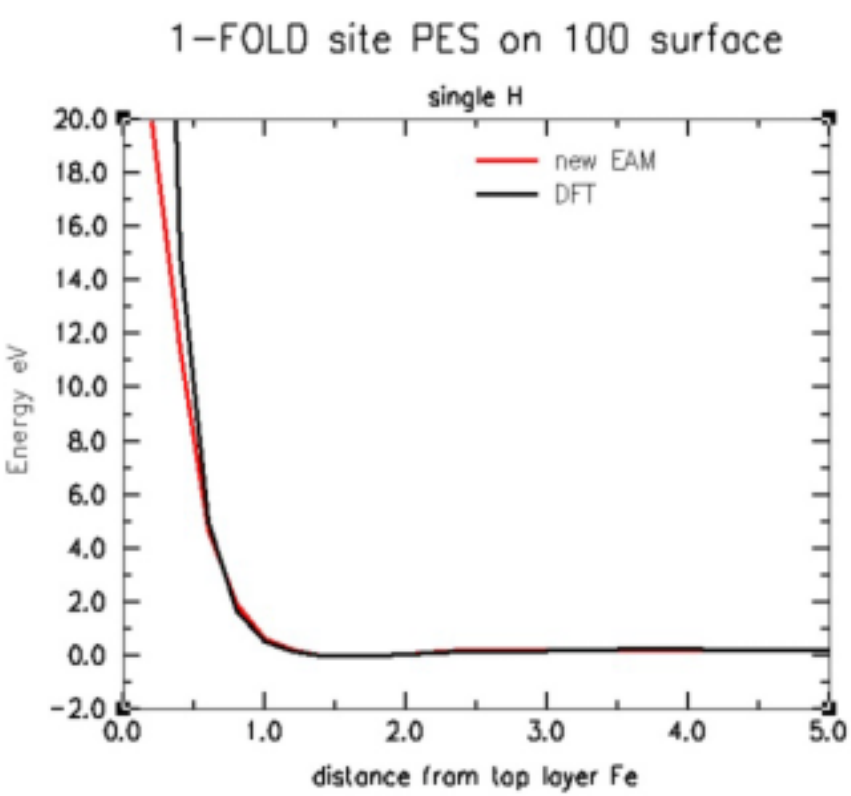
Potential Energy Surface Cut- Farkas Minimum

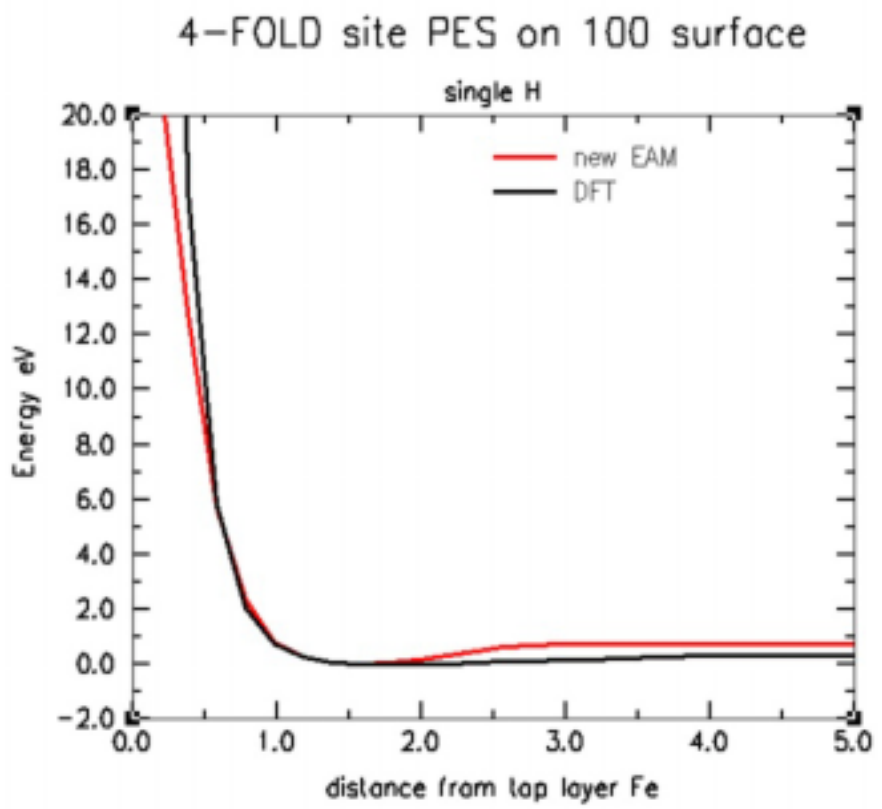






Potential Energy Surface Cut- Did we mess up the 100?

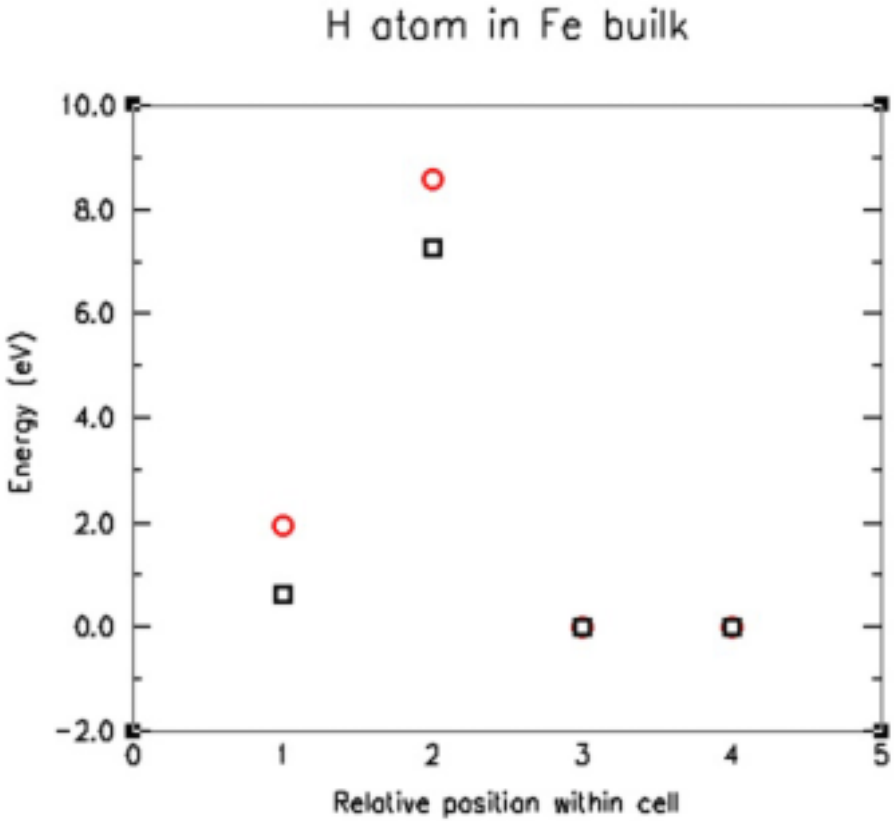


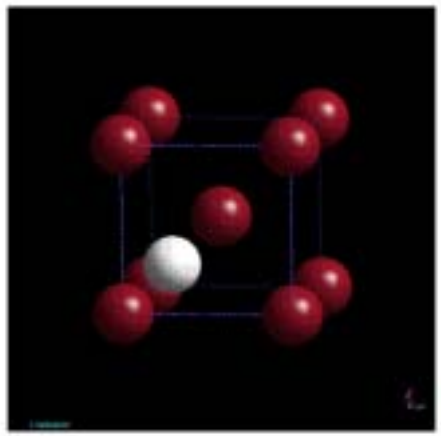


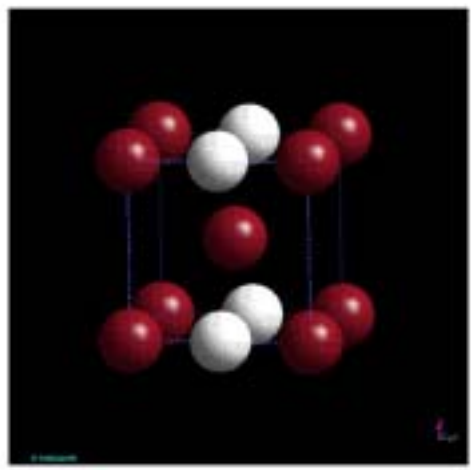
100 looks good

REVISED Potential Energy Surface Cut- Bulk?

So, MUCH better on 111 surface now. How will it work in the bulk?

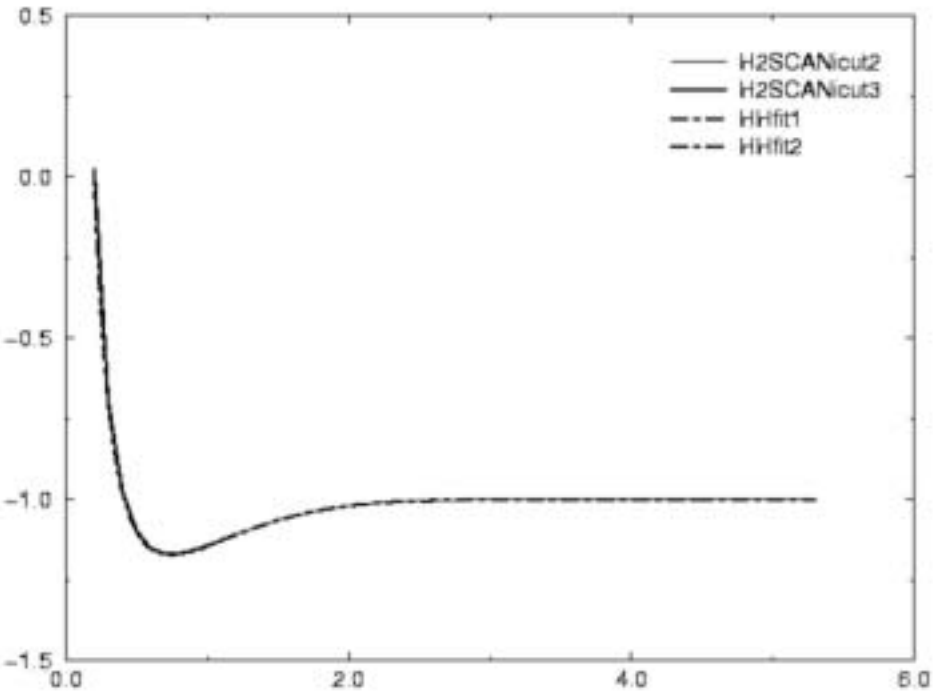






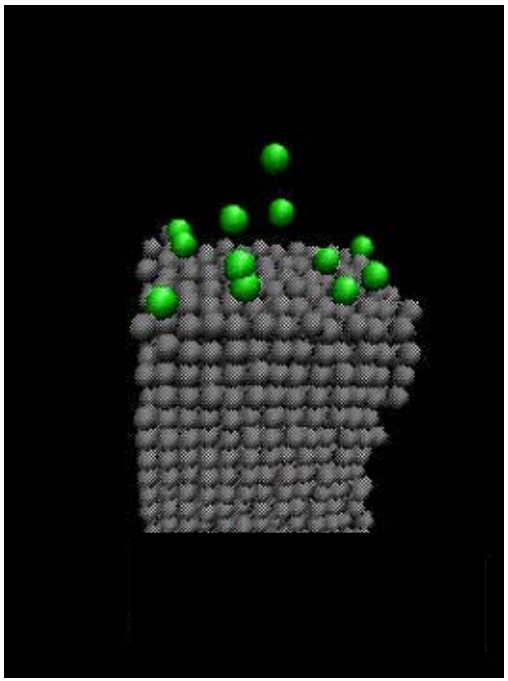
Correct trends, need to improve quantitatively

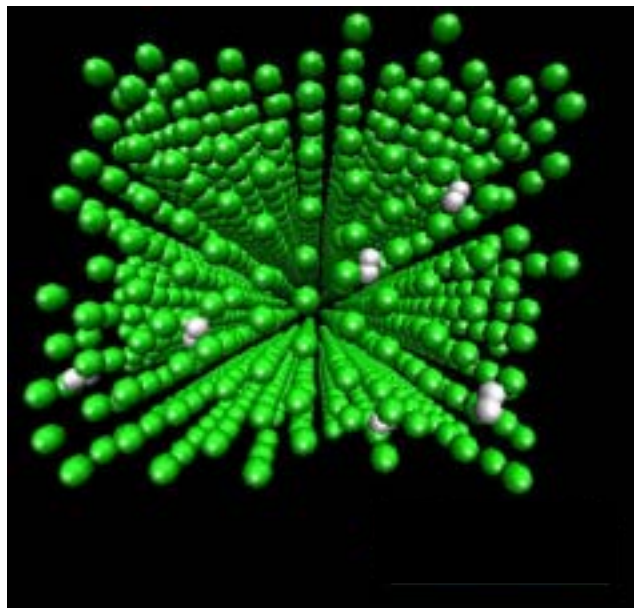
REVISED Hydrogen-Hydrogen Potential

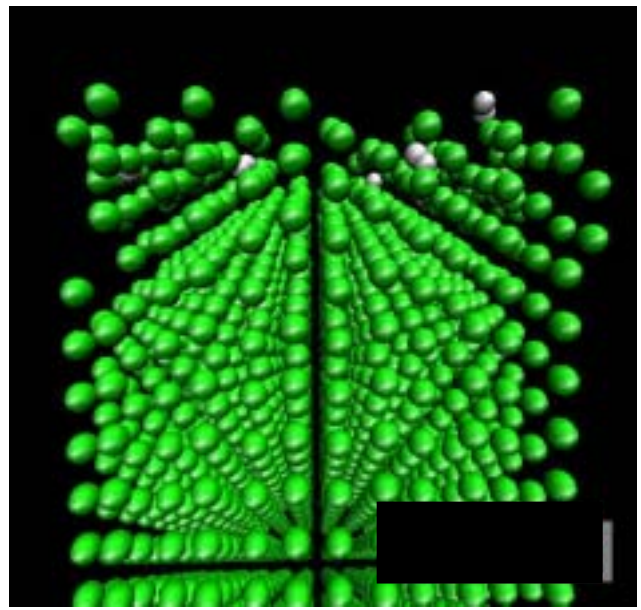


Fit to gas-phase H2 for now

And how does it behave in action?



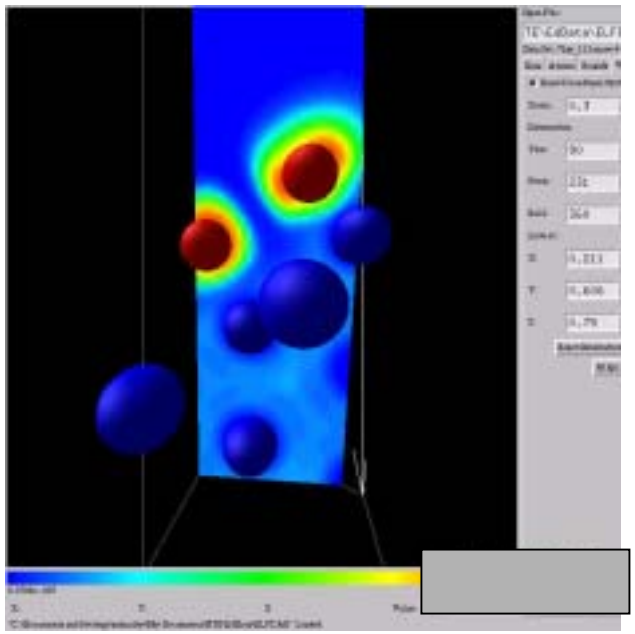




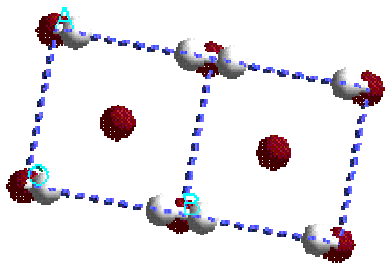
Old potential-
H2 dissociates and floats off

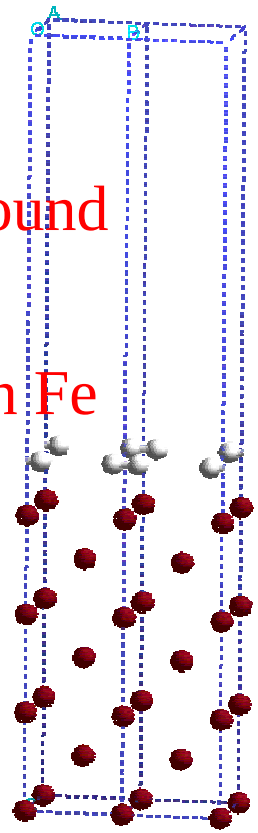
New potential-
Dissociation, reassociation, and diffusion

Ongoing



- H_2 on Fe PES (111) and (100) by DFT
- Tune H_2 on Fe EAM
- O_2 on Fe PES by DFT
- H and H_2 interaction with CO bound on Fe
- O_2 interaction with CO bound on Fe





SUMMARY of Molecular Modeling (to date)

1. **Binding energies for CO on Fe(100):**
   Exp. - 4F > 2F > 1F (PROPOSED)
   Theory- 4F > 1F ≈ 2F-tilt (LOW COVERAGE = 25%)
   4F > 1F ≥ 2F-tilt (HIGH COVERAGE = 50%)

2. **Atomic Carbon binds more strongly than Oxygen at all 3 sites.**

3. **Carbon Embeds Into Matrix, Oxygen Remains Above Surface.**

4. **Embedded Atom Model (EAM) Force Field Improved for H Interacting with Fe (111) Surface; EAM-MD Begun. (Hurley)**

5. **Surface strain (lattice expansion) STABILIZES CO and O absorption, but DESTABILIZES C absorption.**

6. **Barriers to diffusion among 1-F and 2-F sites very small, i.e., ≤ 2 kcal/mol BUT barrier to diffusion from 4-F site is ~13 kcal/mol.**

7. **CO unimolecular decomposition barrier ≈24–28 kcal/mol.; supports exp. interpretation of decomposition competing with desorption at 440K.**

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